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14. ABSTRACT
This work presents the results of an investigation into the role of silica nanoparticle surface chemistry in the enhancement of cyanate ester nanocomposite properties. Previous work has shown that the incorporation of silica nanoparticles improves the thermo-oxidative qualities, moisture uptake properties and processability of cyanate ester resins. This work seeks to better understand the root of these improvements by comparing thermal and mechanical properties as a function of nanoparticle loading and surface treatment using both polar and non-polar as well as potentially reactive surface functionalities. This presentation will focus on the structure-process-property relationships of various silica nanoparticle/cyanate ester systems with a discussion of the implications for novel composite processing techniques.

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Enhanced Cyanate Ester Nanocomposites through Improved Nanoparticle Surface Interactions

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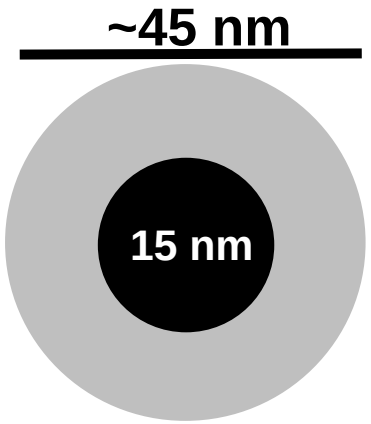
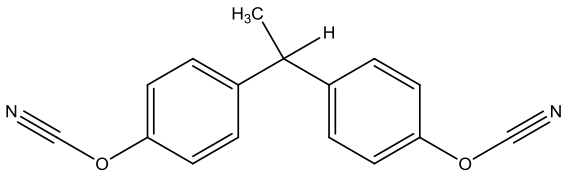
Novel Processing of an Iron(II,III)Oxide/Cyanate Ester Nanocomposite

Induction Coil

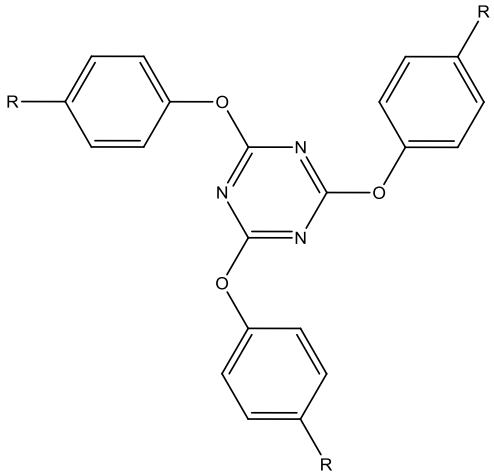
Develop a high-temp nanocomposite that can be 'cured' by induction heating.

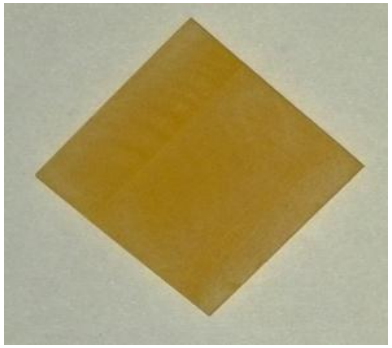


Silica-Coated Magnetite Nanoparticle



LECy

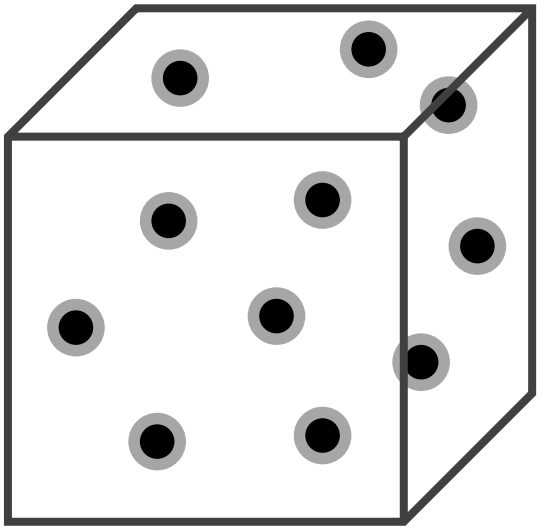




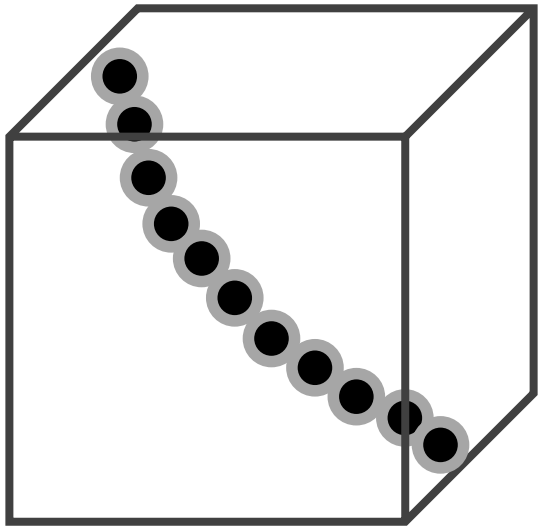
Cured LECy

Multifunctional Structures

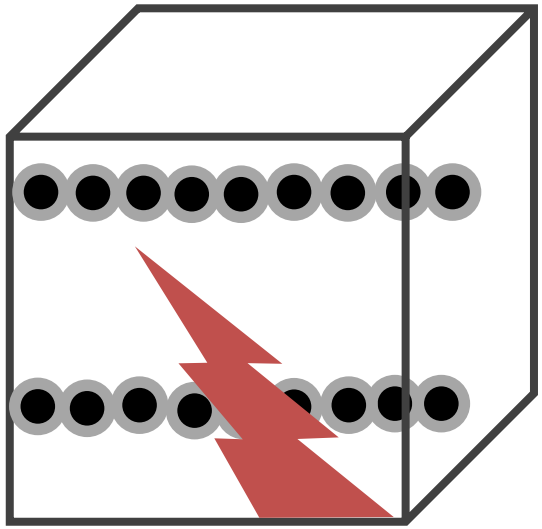
- Controlled molecular network growth
- Multi-functional structures: Energy storage, damage detection, sensors, stimulus response…



Magnetically Seeded Cure



Magnetically Steered Positioning



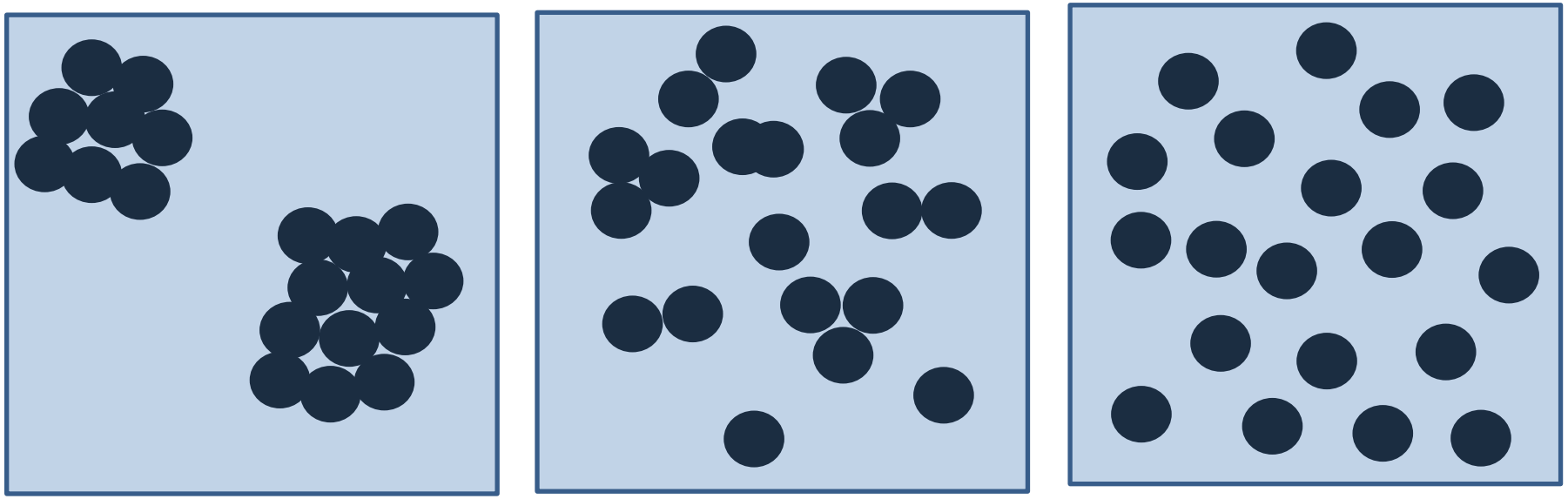
Sensing

Known Unknowns

- **Particle Dispersion**
- **Resin Cure**
  - Is there a catalytic effect?
  - Does this affect the reaction pathway?
- **Heating**
  - Is it sufficient to drive the reaction?
- **Surface Modification**

The Magnetic Nanoparticles

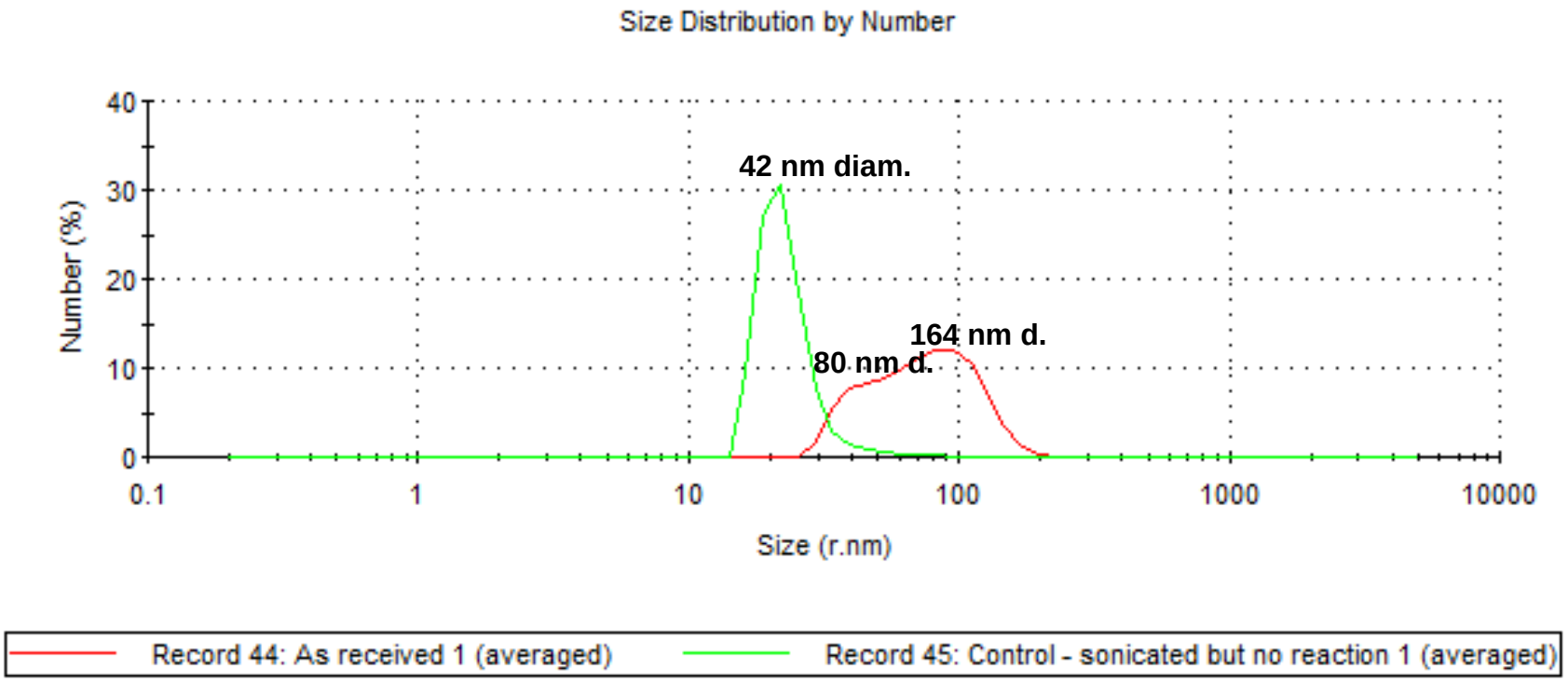
- **Magnetite:** Iron(II,III)Oxide ($FeO \cdot Fe_2O_3$)
- **15 nm nominal diameter**
- **Received in water with no coating/dispersant**



Disperse by sonication

Nanoparticle Dispersion

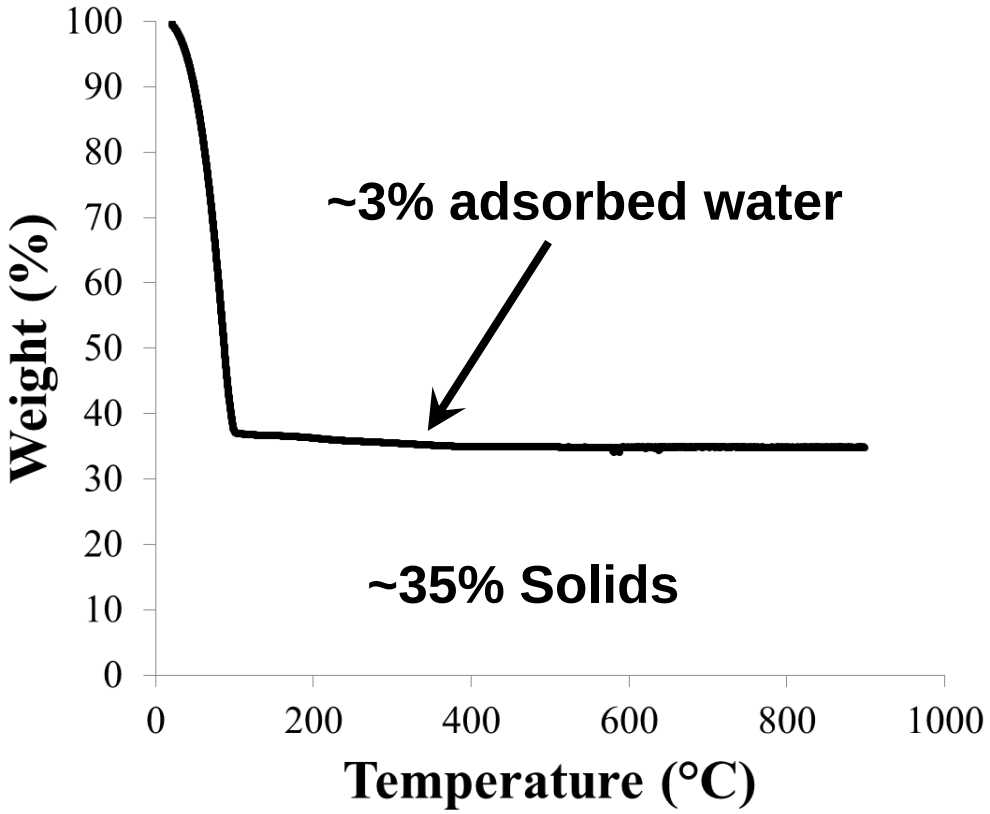
As received (red) vs. diluted and sonicated for 1 hour (green)



Sonication breaks up agglomeration, but not completely.

Water Removal

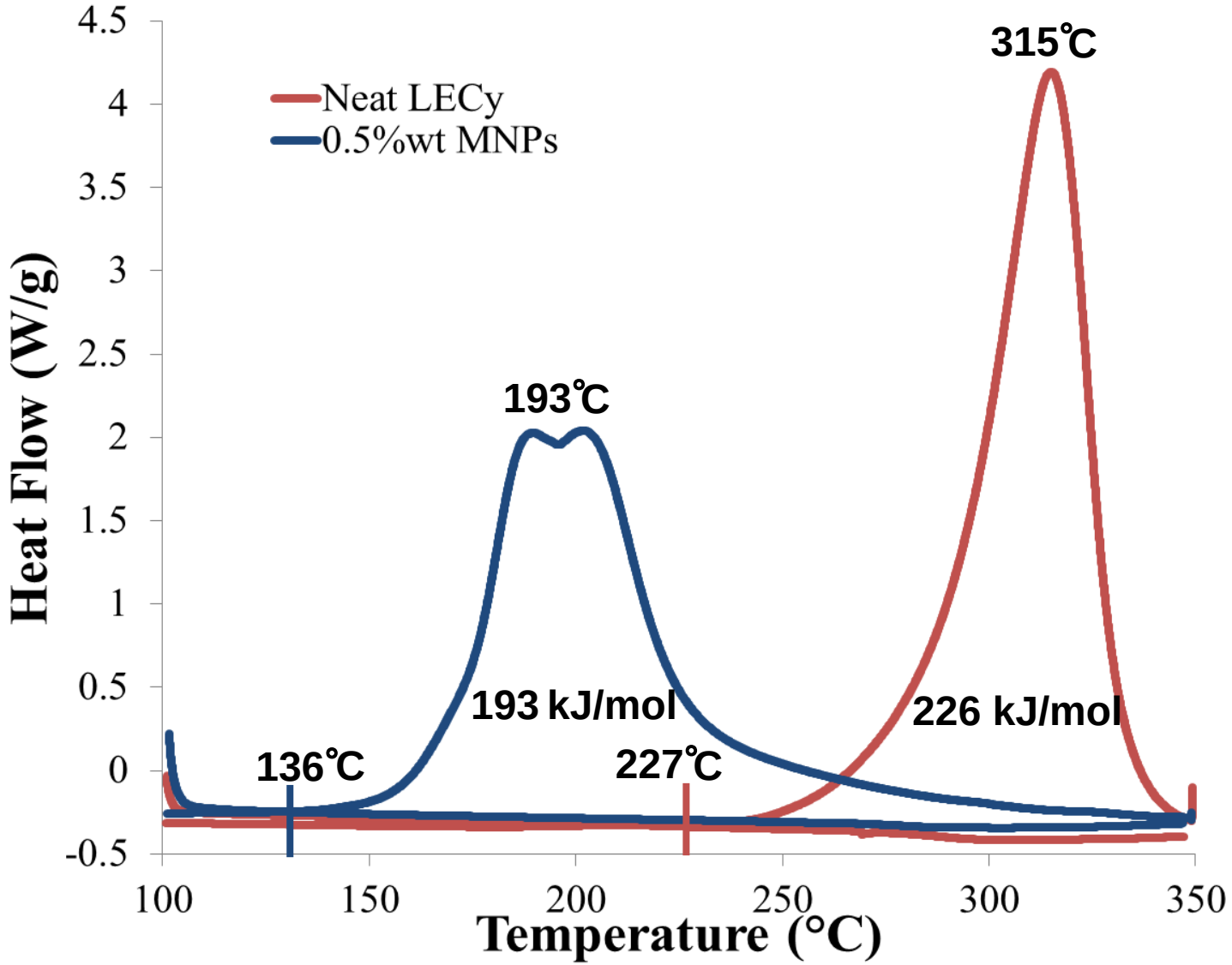
TGA of As-Received MNPs:



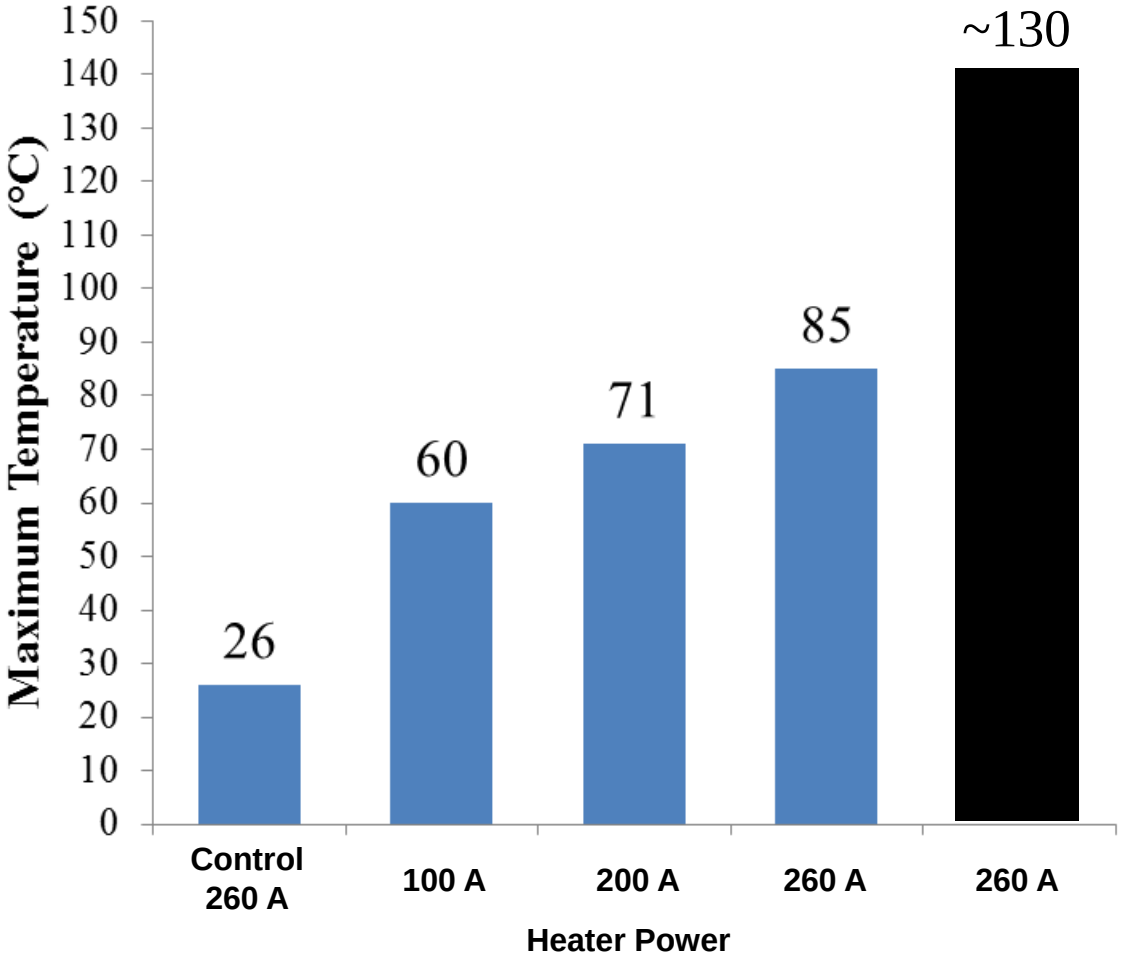
1. Add MNP solution to 20 mL acetone
2. Sonicate for 15 min, separate with magnet then decant
3. Repeat once
4. Add 20 mL dichloromethane
5. Use heat to remove dichloromethane

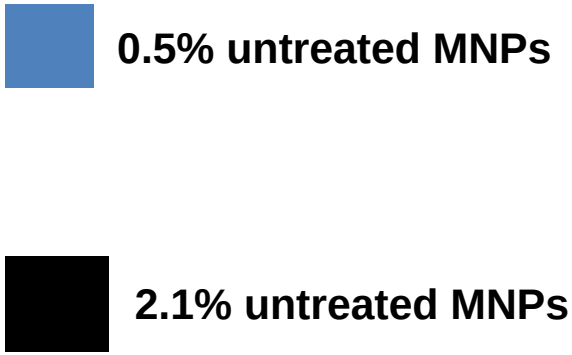
Dichloromethane is easy to remove

The Influence of Unmodified MNPs on Cure



Induction Heating Unmodified MNPs



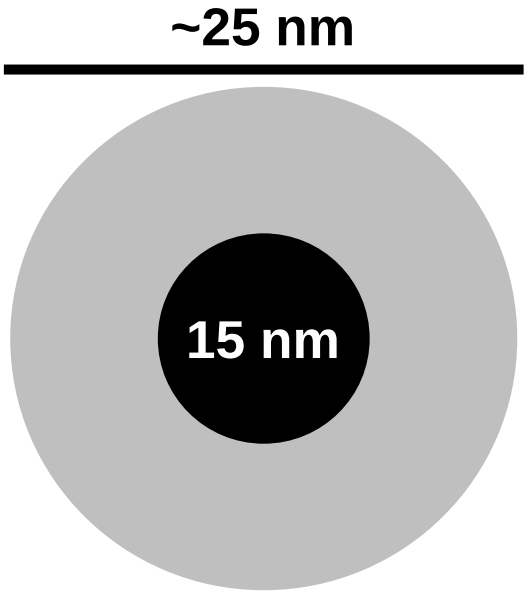


Silica-coated Magnetite Nanoparticles

Unmodified MNPs have a clear catalytic effect on the reaction...

Coat Magnetite with Silica

- **Silica nanoparticles are commonly used to modify physical properties**
- **Iron oxides have unknown impact on curing reaction, long-term performance, etc.**

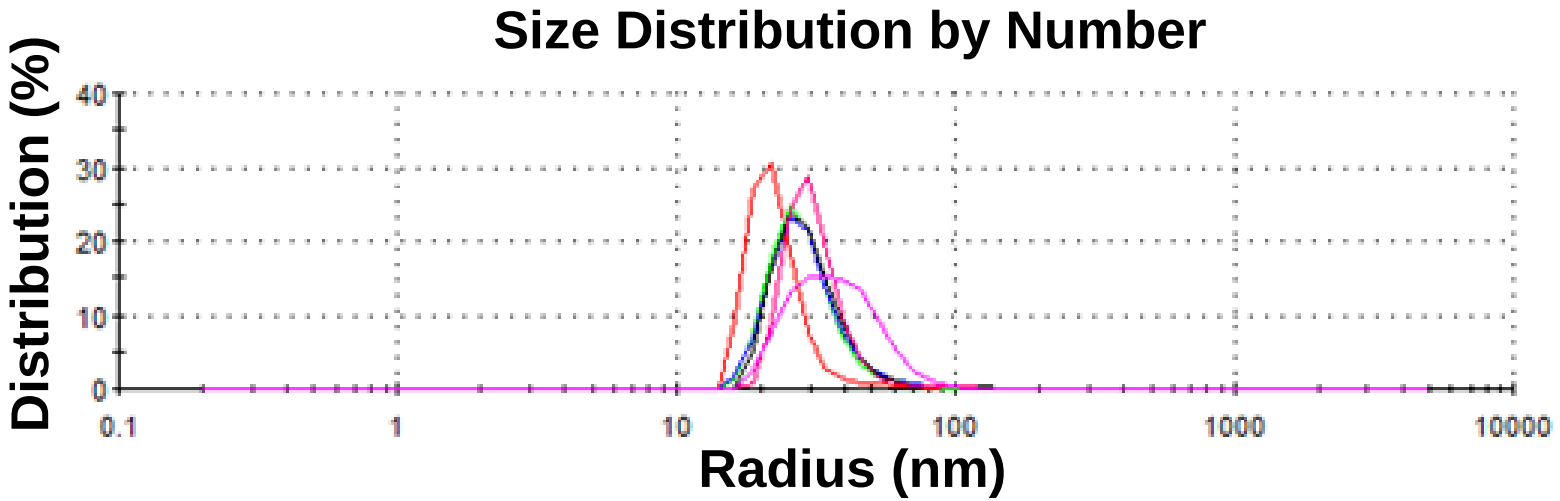


Silica Surface with Magnetite Core

Coating MNPs with Silica

- **Modified Stöber process**
  - Use MNP as a nucleation site
- **Use amount of TEOS to control thickness**
- **Method:**
  1. Rinse 0.1 g MNPs with 0.05 M HCl
  2. Separate with magnet, decant
  3. Rinse with milli-Q water, decant (x2)
  4. Add MNPs with milli-Q water to ethanol to make an 80:20 mix
  5. Sonicate for 3 hours
  6. Add 1 mL of 30% ammonium hydoxide
  7. Slowly add 0.2639 mL TEOS
  8. Allow to react while sonicating solution. Take periodic samples for DLS.

Dynamic Light Scattering

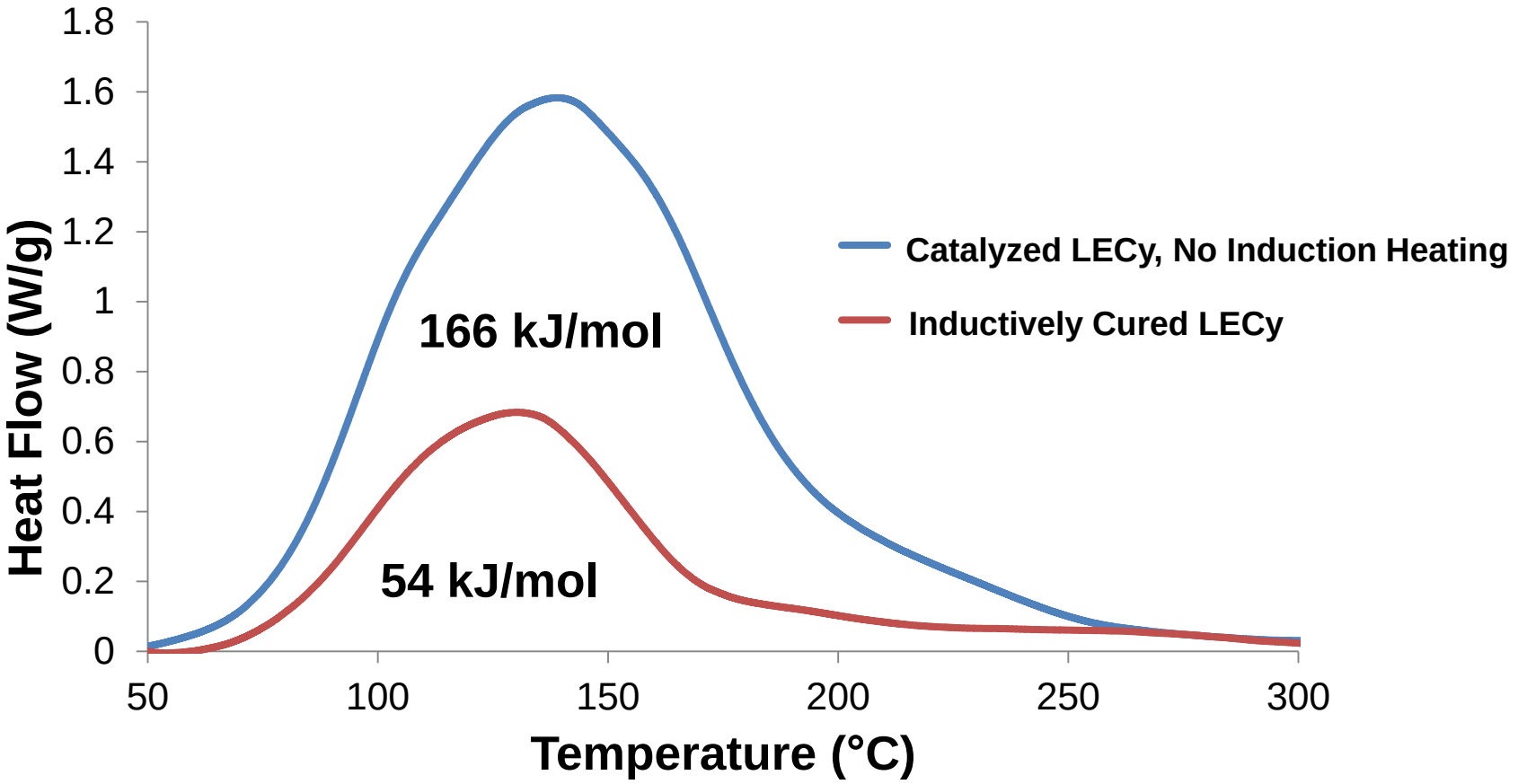


Reaction Time	Diameter (nm)
0 hours	43 nm
1 hour	50 nm
2 hours	50 nm
3 hours	50 nm
4 hours	60 nm
30 hours	70 nm

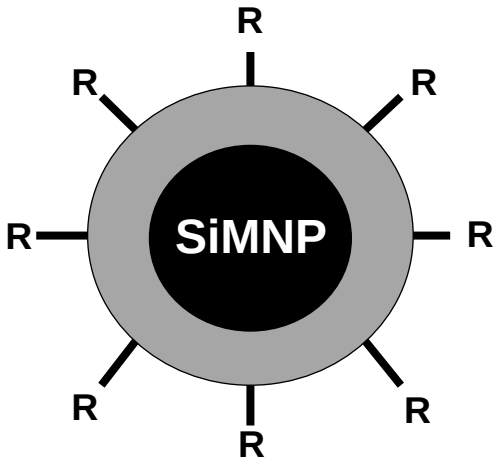
- **Most reaction occurs within one hour**
- **Broad distribution of sizes (still nanoscale)**
- **No TEOS self-condensation**
- **Stable dispersion in EtOH/H_2O**

Resin Cure via Induction Heating

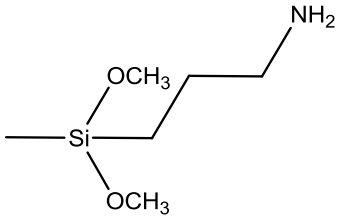
DSC scan of silica modified MNPs (NanoGAP) in LECy



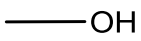
Surface Modification of Silica Nanoparticles



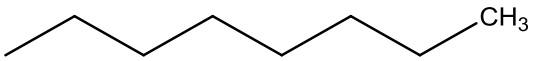
R:



Chemically Active Surface



Hydrophilic Surface



Hydrophobic Surface

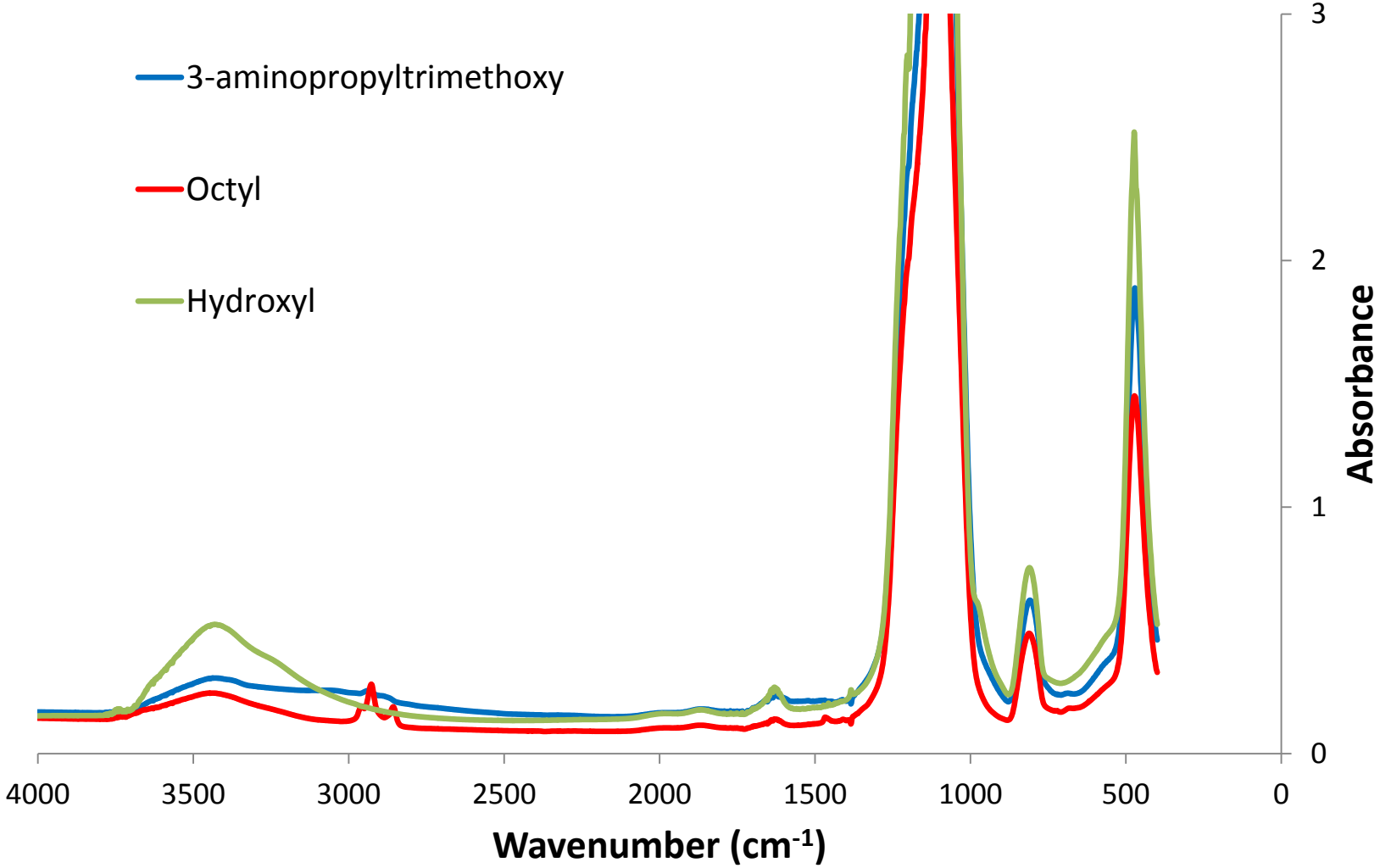
L to R: Octyl, hydroxyl, 3-aminopropyltrimethoxy modified silica nanoparticles. (Evonik)

- **Structure/Processing/Property Relationships**
  - Particle dispersion
  - Reaction Kinetics
  - Glass Transition Temperature
  - Water uptake

Campos; Guenthner; Haddad; Mabry. Fluoroalkyl-Functionalized Silica Particles: Synthesis, Characterization and Wetting Characteristics. *Langmuir*. **2011**, 27, 10206-10215

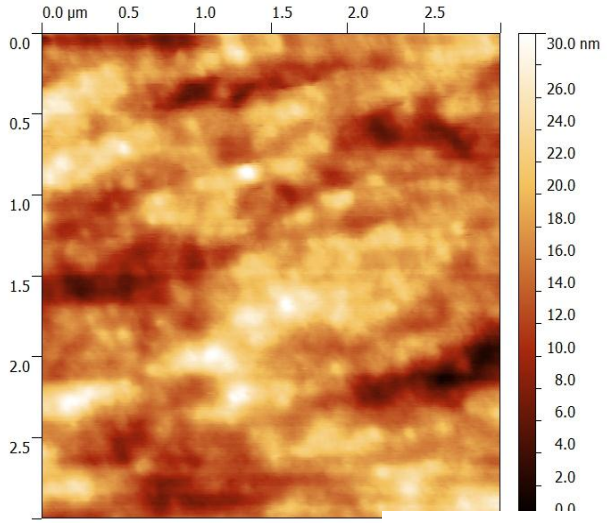
DOI: 10.1021/LA201545A

IR Spectra Showing Modification of Silica Nanoparticle Surfaces

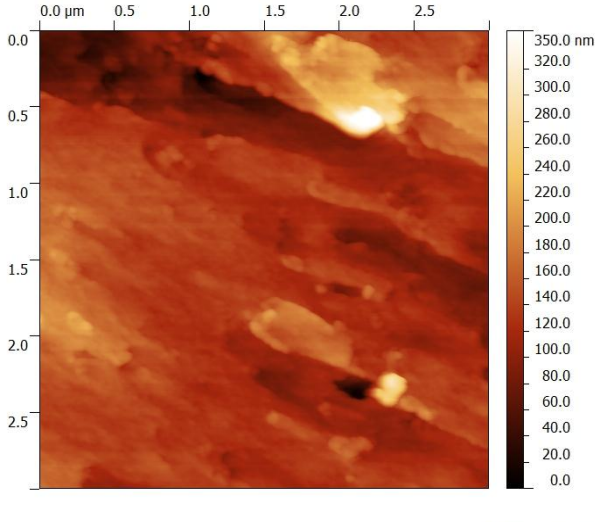


Different Surfaces Show Different Dispersion in LECy

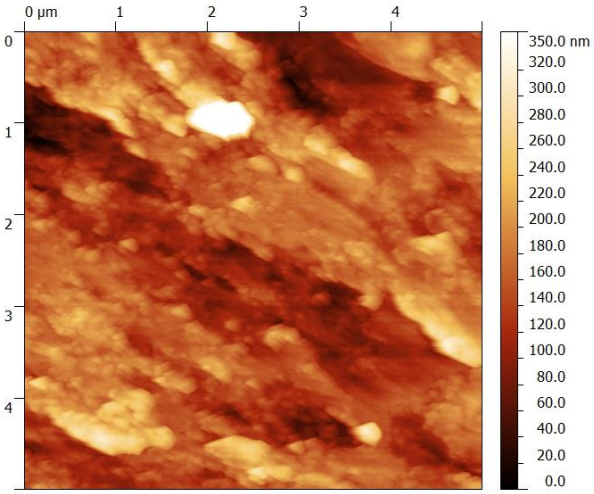
Topographic AFM Images of Sample Fracture Surface:



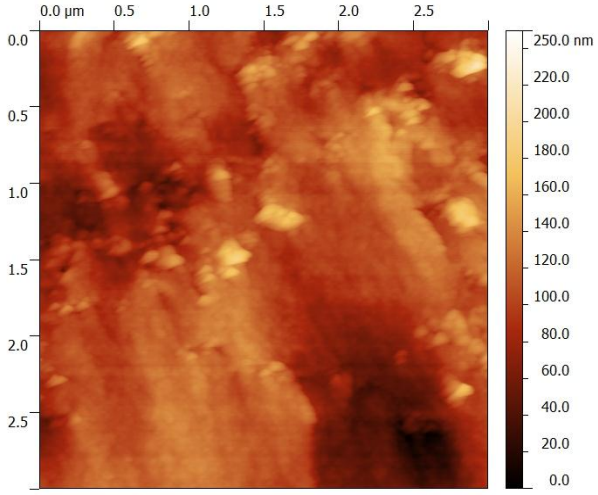
Neat LECy



3-amino

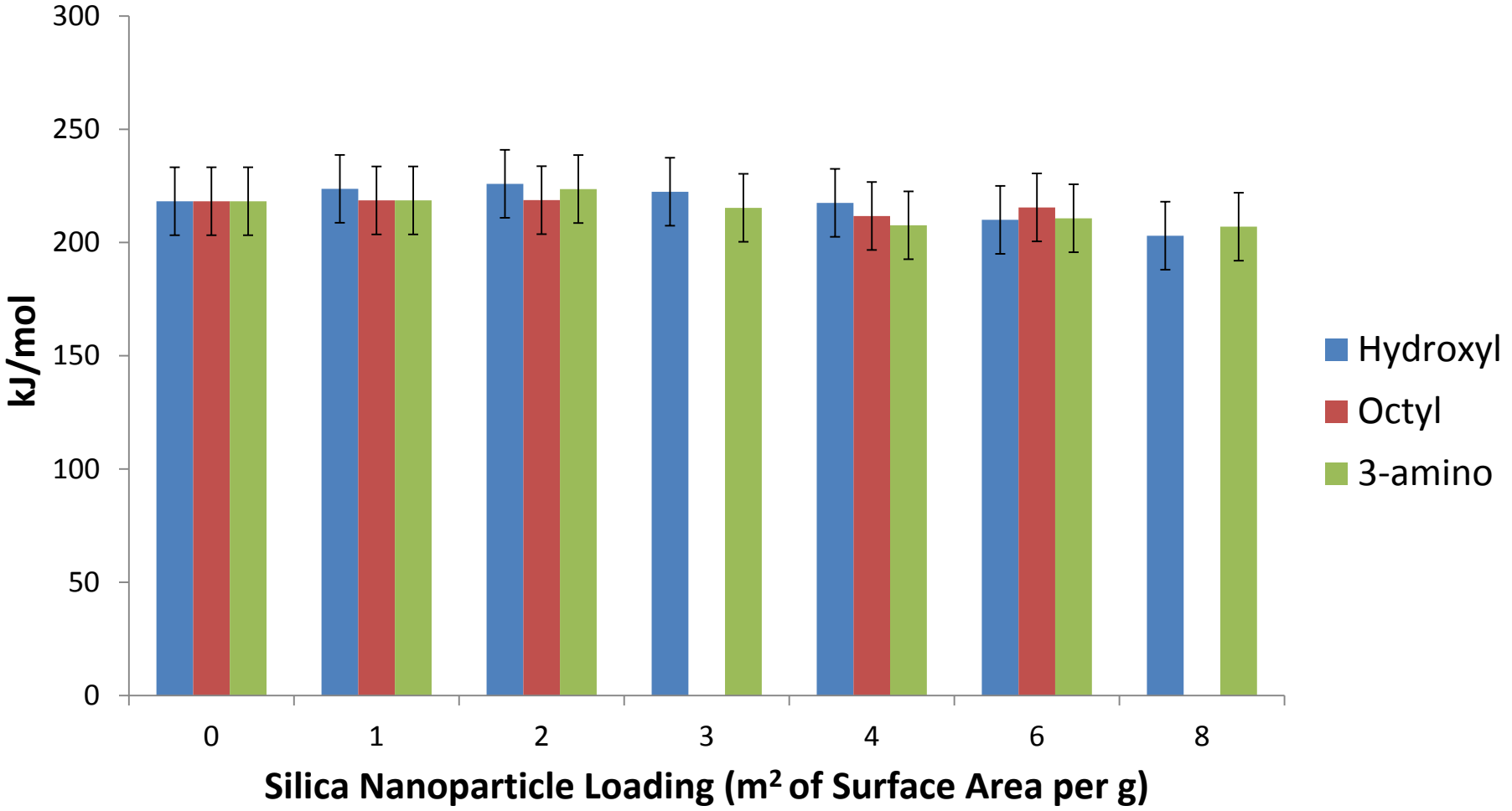


Hydroxyl



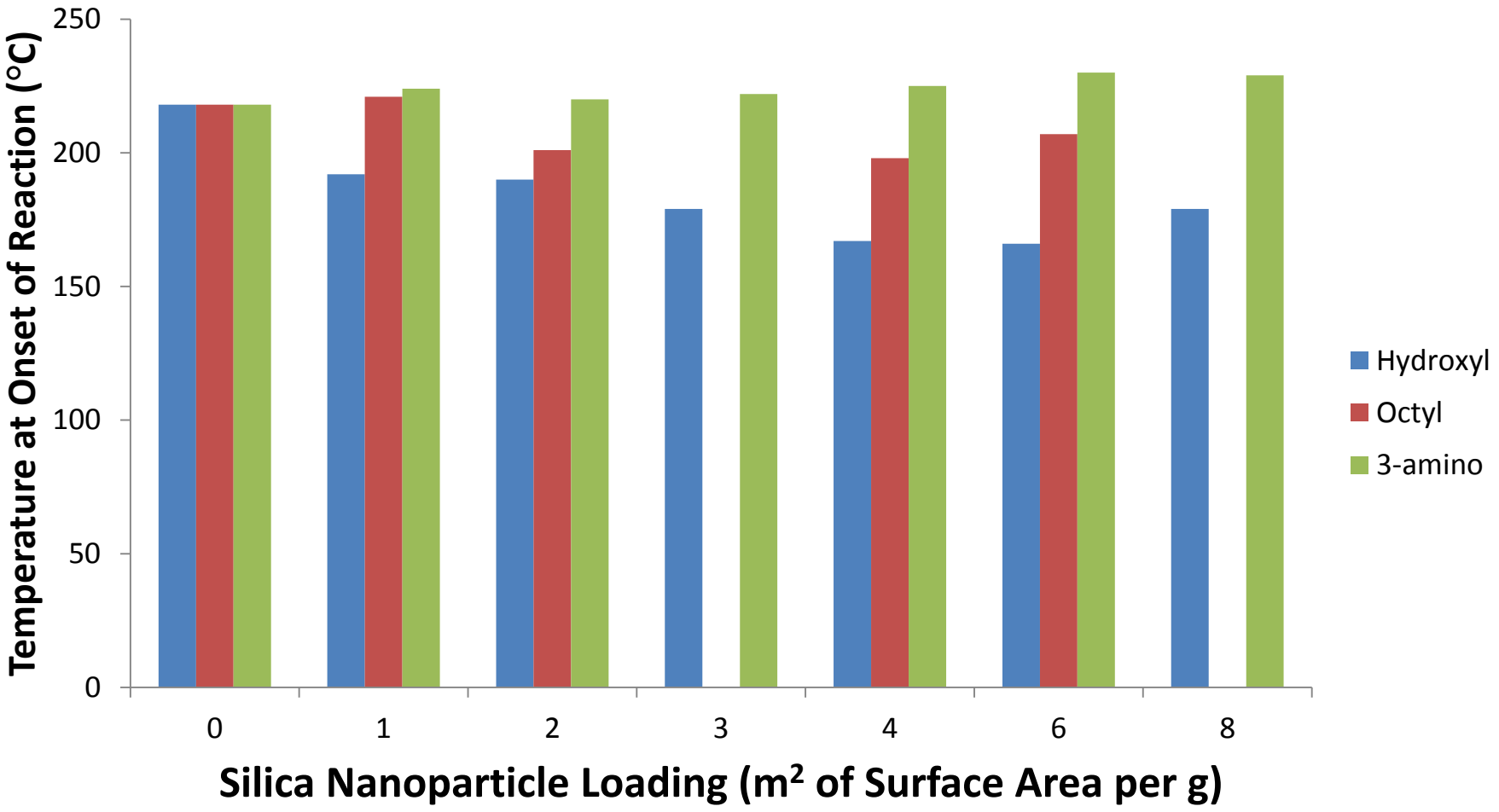
Octyl

Integrated Heats of Reaction



No significant impact on reaction pathway.

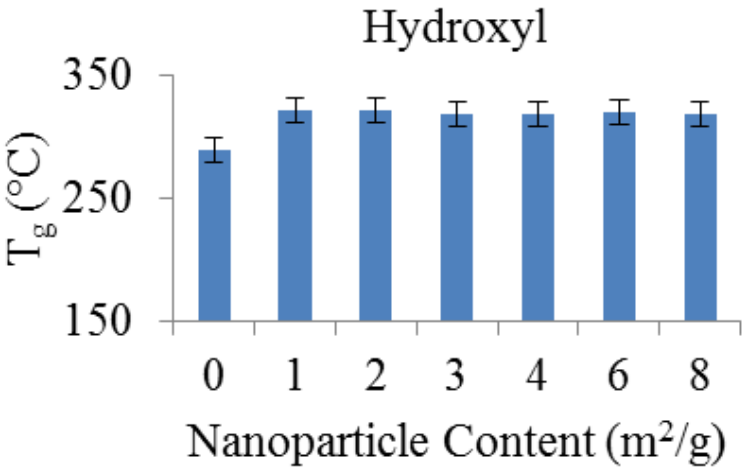
Reaction Onset Temperature

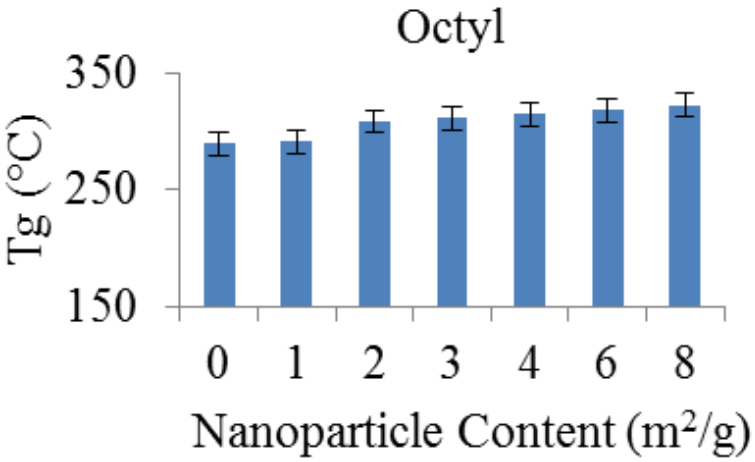


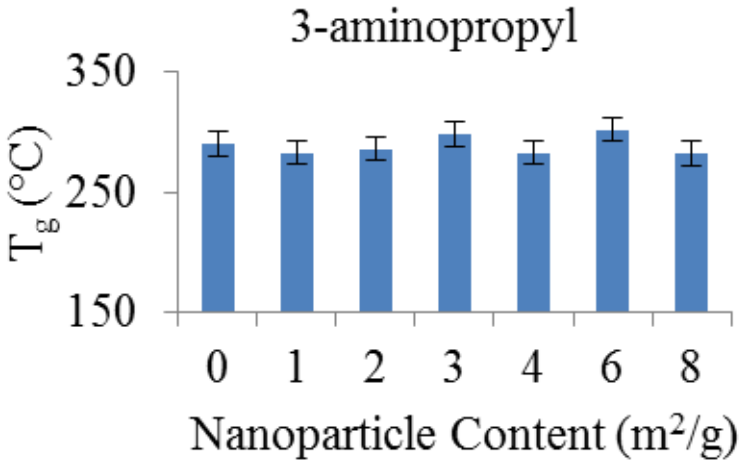
Hydroxyl catalyzes, 3-amino may delay the cure reaction

Glass Transition Temperature of Modified Silica Nanocomposites

Postcured Samples Measured by TMA:







Conversion is more important than surface chemistry

Review

- **Magnetic nanoparticle nanocomposites can enable unique processability and functionality**
- **Lab-scale induction heaters can heat low loadings to well above 100° C.**
- **Silica modification of the MNP surface is straightforward.**
- **No need to further modify the silica surface.**

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